Resonant Small Angle X-Ray Scattering of Polymers at the C-K edge

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INTRODUCTION

Small-angle x-ray scattering is a very valuable technique which complements microscopic techniques by providing statistically averaged information on polymer morphology. For the hard x-rays, scattering intensity is determined by the electron density contrast between two phases [1]. There are situations where this contrast mechanism is not sufficient, e.g. the case where the material has more than two phases or the electron density contrast is not sufficient to give detectable scattering.

We have begun a program to use resonant scattering energies to enhance the information content and signal to noise ratios in small angle x-ray scattering of polymers. Resonant x-ray scattering is a well known phenomenon and has been demonstrated for hard x-ray energies [2], but to our knowledge has never been attempted at the C1s edge, although it has been applied to study magnetic materials [3]. The soft x-ray energy places fairly formidable restrictions on sample preparation conditions. We have performed proof of principle experiments using latex polymers made from polystyrene and polymethylmethacrylate. The early results are very exciting and indicate that this technique may have several interesting and useful applications in the field of polymer characterization.

The x-ray scattering amplitude (f) is a function of energy and is a complex number and the imaginary part (f_2) is due to absorption [4]:

$$f(E) = f_1(E) + i f_2(E) \quad (1)$$

$$f_2(E) = \frac{\sigma_a(E)}{2 r_e \lambda} \quad (2)$$

$$f_1(E) = Z + \frac{1}{\pi r_e hc} \int_0^{\infty} \frac{\varepsilon^2 - \sigma_a(\varepsilon)}{E^2 - \varepsilon^2} \, d\varepsilon \quad (3)$$

The Kramer's Kronig dispersion relation relates the real and imaginary parts, where σ_a is the absorption cross section, λ is the wavelength, r_e is the classical electron radius, h is Planck's constant, c is the speed of light and Z is the atomic number.

Well away from an absorption resonance ($\sigma_a \Rightarrow 0$), x-ray scattering intensity (f^2) is determined by the electron density contrast between the (difference in Z) phases, as mentioned above. Near resonance, however, the intensity is modulated by the absorption cross section. Thus we can make use of the very same near edge x-ray absorption spectral features that have proven useful in x-ray microscopy [5], so-called *near-edge x-ray absorption fine structure* (NEXAFS) [6], to provide chemical contrast between different phases in a polymer system for small angle x-ray scattering experiments. The spectroscopic features, correspond to electronic excited states in which an inner-shell electron has been excited to unfilled molecular orbitals or conduction bands. They are determined by the bonding environment and thus provide a characteristic signature for every material.

The selective enhancement or suppression of the scattering in connection with chemical differences was demonstrated for the carbon C K-edge by using latex spheres of two different chemical compositions (polystyrene and polymethyl methacrylate; PS and PMMA respectively). These lattices were also of different sizes (80nm for PS and 300 nm for the PMMA). In figure 1 we have plotted the scattering intensity (the square of the scattering factor) for the PS and PMMA, calculated from the absorption spectra, using the relationships in equations 1-3.

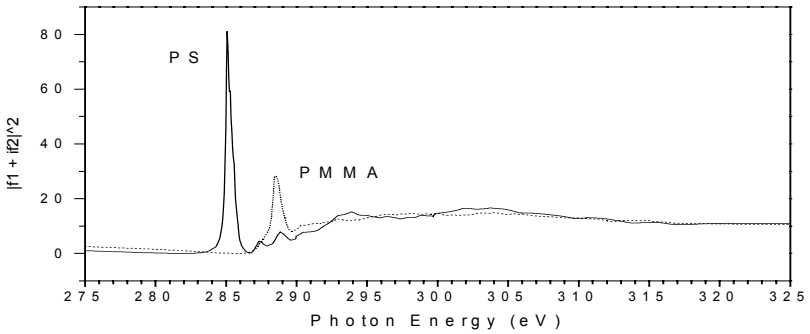

Figure 1. Scattering intensity (f^2) of PMMA and PS calculated from the measured NEXAFS spectra.

RESULTS AND DISCUSSION

NEAXFS spectra were measured from thin films of the lattices dispersed onto thin (100nm) Si_3N_4 windows using the BL7.0.1 scanning transmission x-ray microscope. The most intense peak for both materials is the C1s --> π^* transition which is associated with C=C bonds in PS and C=O bonds in PMMA. Fortuitously, the weakest scattering for each material occurs at energies just below the maximum intensity peak. In Figure 2 the scattering intensity as a function of scattering vector ($q = (4\pi/\lambda)\sin\theta$; θ = scattering angle) is plotted for PS and PMMA samples at the energies for minimum and maximum scattering intensities in each case. The patterns indeed show strong oscillations when measured at the peak scattering intensity and are relatively featureless at the energy of the minimum. In agreement with the relative sizes of the latex particles, one observes that the features in the scattering pattern for PMMA begin at lower q than those for the PS latex. The data can be analyzed by fitting to calculated scattering curves (not shown) and when this is done one retrieves information on particle size consistent with the data provided by the manufacturer measured by other methods. It is interesting to note that deviation of the experimentally acquired data from the calculated pattern occurs and can likely be attributed to the important interfacial or superficial structure of the lattices. This aspect of the data analysis is still under scrutiny by us.

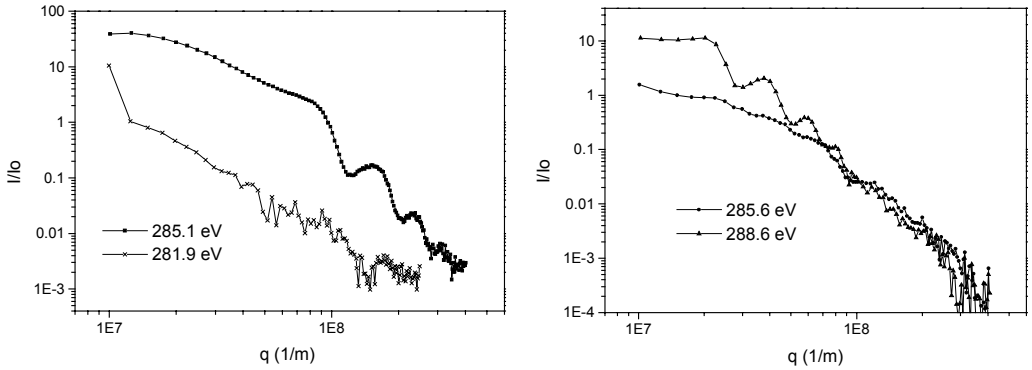

Figure 2. Scattering patterns measured as a function of q for PMMA latex spheres nominally 80 nm in diameter (right) and PS latex spheres nominally 300 nm in diameter (right).

In another experiment, samples of both of the two lattices were randomly dispersed (dried) onto the same Si_3N_4 window. This experiment demonstrates one powerful aspect of this polymer characterization method. When the scattering pattern is measured at 260 eV, well away from any absorption resonances, it appears to be a sum of scattering from both phases. However, at 281.9 eV the scattering from the PS spheres is suppressed and the pattern is dominated by features due to the PMMA spheres. On the other hand, when the data is measured with a photon energy of 285.6 eV the PMMA scattering is suppressed and the pattern is dominated by scattering from PS spheres. Figure 3 shows that in order to determine the structure of one material in the presence of the other, one may acquire the scattering patterns at the energies at which scattering from one phase and then the other phase is enhanced.

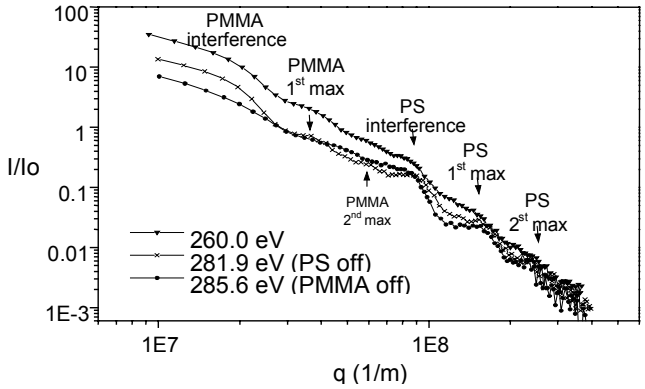

Figure 3. Scattering patterns measured as a function of q for a mixture of the PS latex spheres, nominally 80 nm in diameter and PMMA latex spheres, nominally 300 nm in diameter acquired at the indicated photon energies.

SUMMARY

The presented experiment combines the power of small-angle scattering for sub microscopic structural information with the carbon near-edge absorption fine structure as contrast mechanism for chemical composition. This approach is believed to be useful in several areas where multiphase material are being studied, including polymer blends, structured lattices, soft organic based colloidal materials, advanced electronic materials, structured compound materials, multiphase systems, and nanocomposites.

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